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ABSTRACT

Eltron Research Inc., and team members CoorsTek, McDermott Technology, Inc., Süd Chemie, Argonne National Laboratory, and Oak Ridge National Laboratory are developing an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. This project was motivated by the National Energy Technology Laboratory (NETL) Vision 21 initiative which seeks to economically eliminate environmental concerns associated with the use of fossil fuels. This objective is being pursued using dense membranes based in part on Eltron-patented ceramic materials with a demonstrated ability for proton and electron conduction. The technical goals are being addressed by modifying single-phase and composite membrane composition and microstructure to maximize proton and electron conductivity without loss of material stability. Ultimately, these materials must enable hydrogen separation at practical rates under ambient and high-pressure conditions, without deactivation in the presence of feedstream components such as carbon dioxide, water, and sulfur.

During this quarter, effort was focused on cermet (ceramic-metal) membranes with the general composition $AB_{0.8}B^e_{0.2}O_{3-\delta}$ /44 wt. % metal. Permeation of H_2 increased significantly as the membrane thickness decreased, reaching a maximum permeation rate of ~ 0.5 ml/min/cm² for a 0.8-mm thick membrane at 950°C. Moreover, the improvement in permeation exceeded the 1/thickness dependence predicted by the model. It is anticipated that surface kinetics for H_2 dissociation will begin to limit H_2 permeation as the membrane thickness decreases. Therefore, in an effort to further increase H_2 permeation, 0.8-mm thick cermet membranes were tested with a range of catalysts coatings. However, the best results over the temperature range from 650° to 950°C were obtained for cermet membranes without any added catalysts. Since the cermet composition contains a catalytic metal, it was concluded that an optimal catalyst likely was achieved through intimate mixing of the ceramic and metal phases. Lastly, for this composition it was found that sintering under conditions that were too reductive compromised H_2 permeability.

INTRODUCTION

The objective of this project is to develop an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. This objective will be accomplished by employing dense ceramic and composite membranes based in part on Eltron-patented materials (Patent No. US5821185) with a demonstrated ability for rapid proton and electron conduction. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition and microstructure to enable practical hydrogen separation rates and chemical stability. Other key aspects of this developing technology include catalysis, ceramic processing methods, and separation unit design operating under high pressure. To achieve these technical goals, Eltron Research Inc. has organized a consortium consisting of CoorsTek, McDermott Technology, Inc. (MTI), Süd Chemie, Inc. (SCI), Argonne National Laboratory (ANL), and Oak Ridge National Laboratory (ORNL).

During this quarter, effort was focused on cermet (ceramic-metal) membranes with the general composition $AB_{0.8}B'_{0.2}O_{3.8}/44$ wt. % metal. The dependence of H_2 permeation on membrane thickness and surface catalysis was measured, and additional manufacturing issues affecting performance were identified. Also included in this report are preliminary results from stability testing of selected ceramic and cermet membranes in H_2S , and further developments in thin film fabrication.

EXPERIMENTAL

The Experimental Section of the first quarterly report (January 1, 2001) contained detailed descriptions of equipment and procedures to be used over the duration of this program. The specific aspects presented were: (a) preparation of ceramic powders, (b) preparation of composite materials, (c) fabrication of tube and disk membranes, (d) construction and operation of conductivity apparatus, (e) construction and operation of ambient-pressure hydrogen separation units, (f) construction and operation of high-pressure hydrogen separation units, (g) hydrogen transport and ambipolar conductivity measurements and calculations, and (h) fabrication of thin film ceramics. For brevity, these general issues will not be repeated. However, modification of equipment or methods, as well as any other experimentally relevant issues, will be reported in the Results and Discussion section under their corresponding Tasks as outlined in the original proposal.

RESULTS AND DISCUSSION

Tasks 1 & 2 Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes

Contributors: Eltron, CoorsTek, MTL, SCI, ORNL

a. Membrane Thickness Dependence - Eltron, CoorsTek

Cermet membranes with the general composition $AB_{0.8}B^c_{0.2}O_{3-8}/44$ wt.% metal were used to measure H_2 permeation dependence on membrane thickness. Membranes were prepared with an initial thickness > 3 mm, then sanded down to the desired thickness. Each side was sanded flat, then polished prior to testing. As shown in Figure 1, the two thickest membranes enabled nearly the same permeation rate, and there was actually a slight decrease in permeation from the 1.4- to the 1.2-mm thick sample at 850° and 950°C. Below 1.2 mm, permeation improved significantly and the increase was more dramatic at higher temperatures. For example, the 1-mm thick membrane enabled H_2 permeation rates of 0.13 and 0.17 mL/min/cm² at 700° and 950°C, respectively. However, the 0.8-mm thick membrane achieved 0.47 mL/min/cm² at 950°C, compared to only 0.21 mL/min/cm² at 700°C.

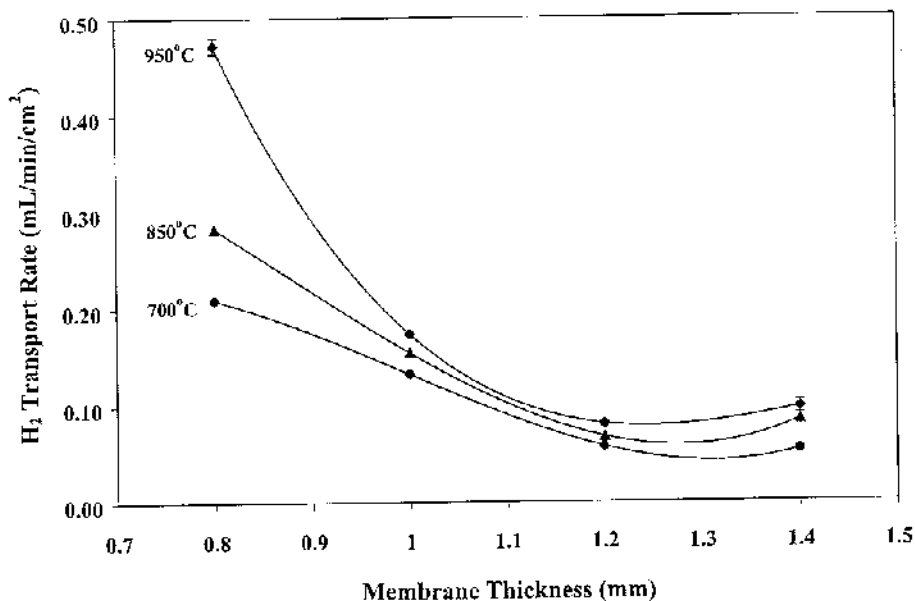


Figure 1. Plot showing the relationship between cermet membrane thickness and H_2 permeation rate. The general membrane composition was $AB_{0.8}B^c_{0.2}O_{3-8}/44$ wt.% metal. The inlet gas was 80 vol.% H_2 (humidified, bal. He) and the sweep gas was Ar.

Although there was a clear dependence of permeation rate on membrane thickness, the increase in permeation exceeded that predicted by the relationship $J = \sigma V/t$ (J = flux, σ = bulk conductivity, V = Nernst potential, t = membrane thickness). The results in Figure 1 indicated that the permeation process is largely diffusion limited. However, it is also very likely that surface kinetics contribute to permeation for the thinner membranes. It was observed previously that during sintering, the metal phase migrates from the membrane interior to the membrane surface. Therefore, it is possible that the distribution of the metal phase through the thickness of the membrane was not perfectly homogeneous, and sanding samples to different thicknesses resulted in different surface catalyst characteristics. SEM measurements of the surfaces of membranes used for this study currently are being conducted to address this issue.

b. Effect of Catalyst on Hydrogen Transport Rates - Eltron, SCI

In the previous report it was indicated that a catalyst improved H_2 permeation for thick ceramic membranes (≥ 1 mm), but that the difference between catalysts was negligible. It was suggested that H_2 permeation for thick membranes was primarily limited by proton transport, and thus not particularly sensitive to surface kinetics. During this reporting period, catalyst testing was continued using thinner membranes and a cermet rather than a ceramic membrane.

The membrane composition used for testing is represented as $AB_{0.8}B^c_{0.2}O_{3.3}/44$ wt.% metal, and all samples were sanded down and polished to a thickness of 0.78 ± 0.02 mm as described above. Catalysts used for these tests were Pt, Pd, Ni/ceramic slurry, and a porous layer of the cermet material. The Pt catalyst was applied by sputter coating. Pd was applied by dropwise addition of a palladium acetate/acetone solution, followed by drying, and reducing under testing conditions. The Ni/ceramic slurry was prepared by wet impregnating an ABO_3 powder with an aqueous $Ni(NO_3)_2$ solution, followed by drying and reducing under H_2 . An alcohol slurry was prepared from the resulting powder and painted onto the membrane surface, followed by drying and curing under testing conditions. The porous cermet catalyst was prepared as a slurry of the membrane powder in solvent with a binder added. The slurry was painted onto the membrane, dried, then cured under testing conditions.

Results from catalyst testing are summarized in Figure 2. The Pt and Pd catalysts produced almost identical results, and the porous cermet catalyst was only slightly better. The best results were obtained for the sample with no catalyst added, however, the metal phase of the cermet actually has high catalytic activity for H_2 dissociation. The Ni slurry catalyst performed well at higher temperatures, unfortunately the seal was lost as the temperature was decreased below $850^\circ C$. SEM images of the membrane surfaces are shown in Figure 3. The metal phase (dark region) is clearly seen in the image of the bare membrane, and the edges of the metal phase appeared raised slightly above the surface. The Ni/ceramic and porous cermet catalysts looked similar, but the latter appeared to have greater surface roughness. The Pd and Pt catalyst each consisted of discrete metal islands, but the Pt catalyst annealed into very large agglomerates. After testing, the catalyst films appeared the same on the inlet and sweep sides of the membrane, except for the Pt catalyst, which showed much less metal annealing on the sweep side than the H_2 side.

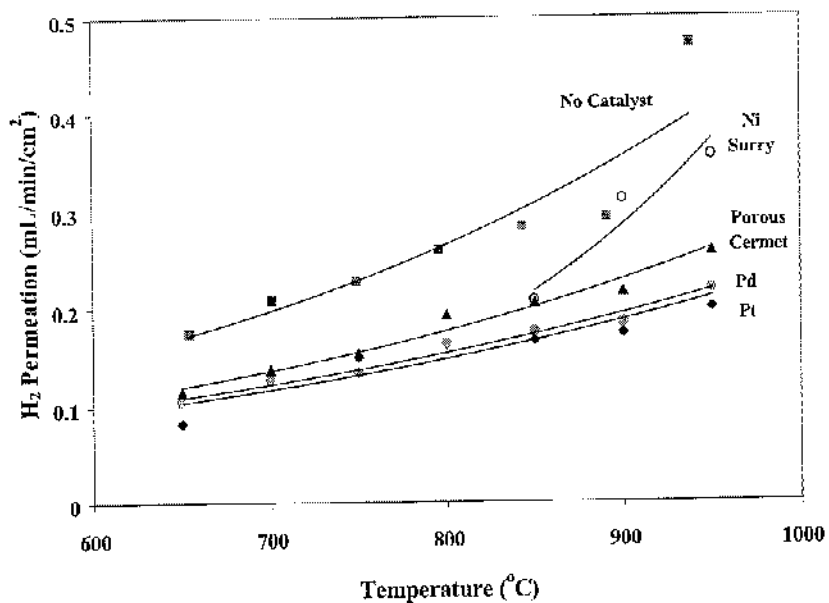


Figure 2. Plot showing H₂ permeation as a function of temperature for 0.8-mm thick cermet membranes with various catalyst coatings.

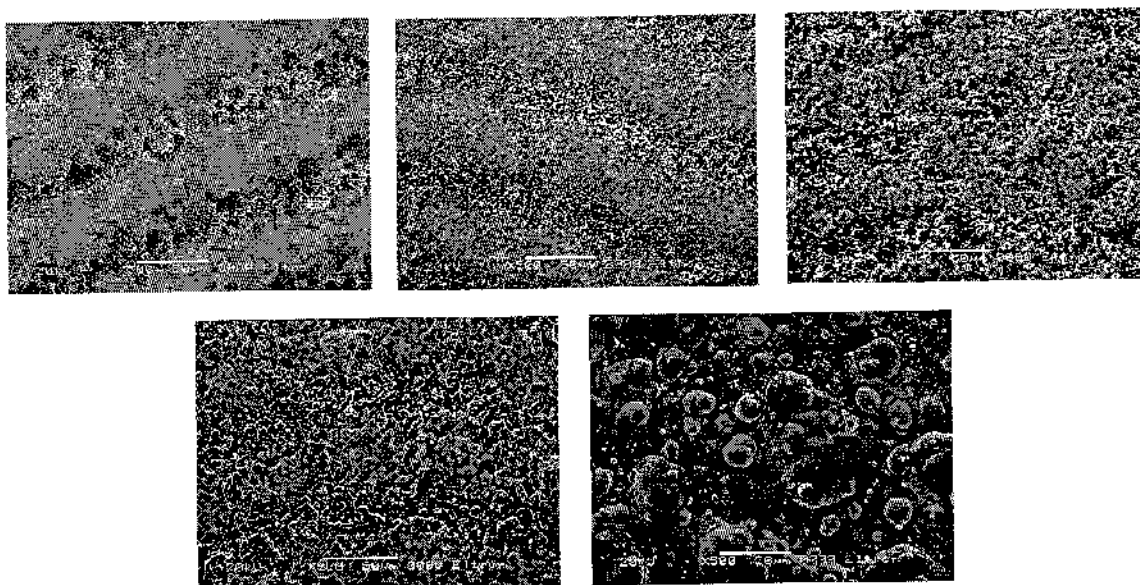


Figure 3. SEM images of catalysts deposited onto cermet membranes. From left to right, top to bottom, the images were of a bare cermet, Ni/ceramic, porous cermet, Pd, and Pt catalysts.

Overall, adding catalysts to the cermet membranes reduced H_2 permeation. For permeation to proceed, H_2 must be dissociated into protons and electrons at the membrane surface, and protons must be transferred into the membrane lattice. Therefore, for this application, catalytic activity anywhere but directly on the membrane surface is not expected to improve permeation. For the Pt catalyst, it is possible that any catalytic benefit at the surface was offset by Pt masking membrane lattice surface sites. Similarly, it is possible that adding a porous cermet layer actually increased the effective membrane thickness. However, this same effect would be expected for the Ni/ceramic catalyst as well. Furthermore, due to high mobility of H_2 in Pd, it was surprising that this catalyst suppressed permeation so significantly. Ultimately the catalytic activity of the cermet metal phase intimately mixed with the ceramic produced the best results.

c. Manufacturing Issues and Relative Economics - CoorsTek, Eltron

Sintering of cermet compositions is performed under reductive conditions (*i.e.*, H_2) to avoid oxidation of the metal phase. To improve the safety and economics of this manufacturing step, it is desirable to maintain the H_2 concentration as low as possible. Accordingly, the effect of the sintering atmosphere on cermet membrane characteristics was determined at CoorsTek by sintering a selected composition using nitroenal gas (25% H_2 /bal. N_2) and forming gas (3% H_2 /bal. Ar).

The membrane composition used for these tests is represented as $AB_{0.8}B^c_{0.2}O_{3.8}/44$ wt.% metal. XRD analyses of each sample revealed both the ceramic and metal phases. However, the XRD pattern of the ceramic phase for the sample sintered under forming gas was identical to the parent ABO_3 ceramic, whereas the sample sintered under nitroenal demonstrated peak broadening and shifting. These results indicated a greater degree of crystallographic distortion from cubic symmetry for the sample produced under more reductive conditions, which is consistent with a greater degree of oxygen vacancies.

SEM images (not shown) of samples sintered under both gases clearly demonstrated distinct regions of metal phase several microns in diameter surrounded by the ceramic phase. Although continuity of the metal phase was not apparent in the two-dimensional SEM images, continuity was confirmed using ohmmeter measurements across the membrane surface. The perimeter of each region of metal phase contained a boundary layer roughly $1 \mu m$ in thickness. EDX measurements of the boundary layer indicated diffusion of the metal phase into the ceramic phase. The extent of metal diffusion was nearly equivalent for both samples, but possibly a little greater for the sample sintered under nitroenal. Additionally, the sample sintered under nitroenal had a slightly smaller grain size, and demonstrated intergranular fracture on SEM fracture cross section analysis.

The $AB_{0.8}B^c_{0.2}O_{3.8}/44$ wt.% metal samples prepared by CoorsTek were tested at Eltron for H_2 permeation, and the results are presented in Figures 4 and 5. For comparison, results for the same composition prepared at Eltron and sintered under 10 vol.% H_2 (bal. Ar) also were included. As indicated in the figures, the sample sintered under forming gas had considerably higher H_2 permeation and corresponding mixed proton/electron (apparent) conductivity than the sample sintered under nitroenal. Furthermore, results from the Eltron sample supported the apparent relationship between H_2 concentration during sintering and resulting H_2 permeation (of course, differences between the Eltron and CoorsTek samples might reflect other subtle variations in membrane preparation). These results were consistent with the characterization data, and it is concluded that the higher H_2 concentration during sintering creates more oxygen vacancies that distort the ABO_3 lattice and lead to inhibited grain growth and weaker grain boundaries. These

factors lead to asymmetry, which likely decreases H_2 permeation by creating unequal lattice sites along the proton conduction pathway.

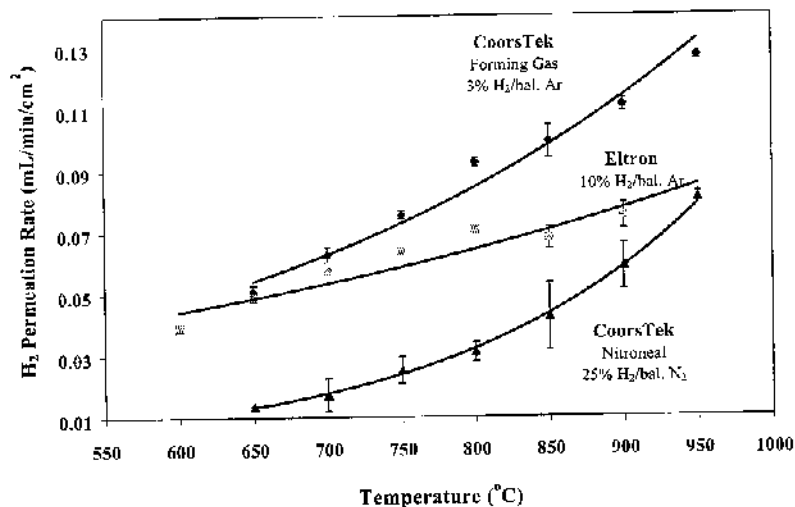


Figure 4. Plot showing H_2 transport versus temperature for samples sintered under different H_2 concentrations (vol.%). Testing was performed with humid 80 vol.% H_2 (bal. He) on the inlet, and a sweep of Ar on the outlet. Membrane thicknesses were > 1 mm.

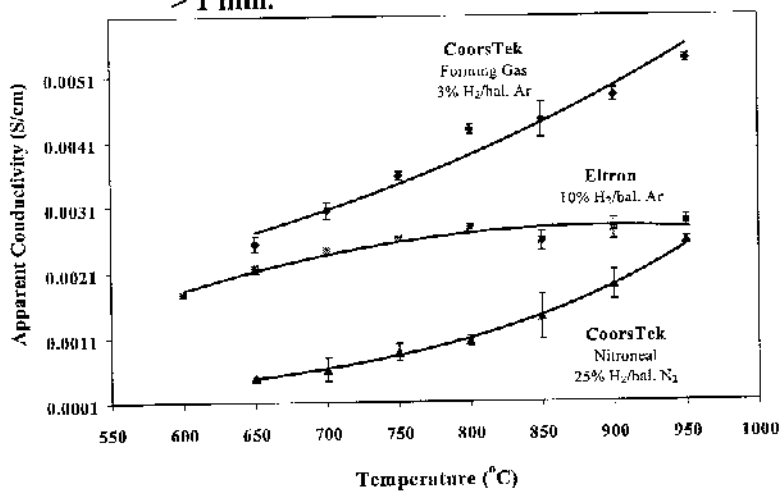


Figure 5. Plot showing mixed proton/electron (apparent) conductivity versus temperature for samples sintered under different H_2 concentrations (vol.%). Testing was performed with humid 80 vol.% H_2 (bal. He) on the inlet, and a sweep of Ar on the outlet. Membrane thicknesses were > 1 mm.

d. Membrane Stability in Reactive Gases - Eltron

Numerous permeation tests performed over a range of temperatures for up to two weeks at a time have indicated that these membranes are stable in H_2 and can tolerate very reductive conditions. These same tests also indicated that these materials are stable in moisture under operating conditions. Other potentially reactive gases present in Vision 21 energy plants include, CO , CO_2 , and H_2S , and the concentrations of these species will depend on the location within the processor (*i.e.*, before or after catalyst units or moisture condensers). Using coal gasification as a model process, typical values for these gases (volume percent) after sulfur removal are roughly 46% H_2 , 47% CO , 6% CO_2 , 0.02% H_2S , and 0.34% H_2O . However, prior to desulfurization, H_2S can be as high as ~0.9%, or 9,000 ppmv. As indicated in the last report, information compiled by MTI indicated that membrane sulfur tolerance is the primary factor that will determine where the H_2 separation unit will be placed within the energy plant. Accordingly, testing has been initiated to assess the effect of H_2S on membrane characteristics.

Candidate membrane compositions were placed in a cell under flowing H_2S (1000 ppmv/bal. N_2) at 950°C for 72 hours, and XRD patterns before and after exposure were used to determine the extent of reaction. All compositions tested clearly demonstrated reaction with H_2S , although the original perovskite diffraction pattern remained as well. Compositions of the form $\text{AB}_{0.8}\text{B}'_{0.2}\text{O}_{3-\delta}$, where B' is one of seven transition metals, generally showed formation of the sulfide of the A-site cation, AS, and the B-site oxide, BO_2 . Oxides of the B' dopant also were observed in some cases, $\text{B}'\text{O}_x$, or oxides of the form $\text{AB}'\text{O}_3$. Two different compositions of the form $\text{AB}_{1-x}\text{B}'_x\text{O}_{3-\delta}$, where $0.05 \leq x \leq 0.8$, also were tested with similar results. Finally, cermets of the form $\text{AB}_{0.8}\text{B}'_{0.2}\text{O}_{3-\delta}/44$ wt.% metal also were tested. The effects of H_2S were not as obvious, however, peaks associated with sulfides of the A-site cation and the metal phase were clearly present.

Although the implications of these results for H_2 permeation under real conditions is not yet known, these tests definitely suggest desulfurization will be necessary prior to hydrogen separation.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

Operation of dense ceramic hydrogen separation membranes at high temperatures and pressures requires a chemically resistant seal with similar mechanical and expansion characteristics as the membrane material. During this quarter, seal composition testing was continued and complemented with coefficient of thermal expansion measurements. Seal formation was achieved by ramping the cell assembly up to 1000°C and holding for a period of time. The assembly then was cooled to 800°C for seal testing. Seals tested during this quarter enable a pressure of 100 psig to be maintained, which was equivalent to the best results achieved previously.

Task 4 *Thin-Film Hydrogen Separation Membranes*

Contributors: Eltron

Attaining adequate seals for evaluation of thin films is proving still to be very difficult. For thicker membranes, pressure can be applied to promote seal formation at temperatures above the seal material softening point. However, thin films are comparably fragile, and applied pressure sufficient for seal formation results in membrane cracking. To circumvent this problem, temperatures for seal formation have been raised so that the seal material will melt and wet the interface between the membrane and inlet tubing. Good seals were achieved using this method, unfortunately the seal materials wet a large portion of the membrane, leaving only a very small area of membrane exposed. As a result, measuring membrane area was difficult and H₂ permeation rates appear roughly equivalent to thick membranes (*i.e.*, ~ 0.1 to 0.2 mL/min/cm²). During the next quarter, the approach will be to use very thin rings of seal material, and insure that the membrane surface and inlet tubing make complete contact.

Additional work was performed to optimize the support porosity and the shrinkage rates of the support and thin film. Two different organic materials were used to generate pores in the thin film support, and the materials had opposite effects on the support shrinkage during sintering (*i.e.*, one material increased support shrinkage with increasing concentration and the other material decreased shrinkage). Despite these trends, support porosity demonstrated a maximum at approximately 23 wt.% of added organic material. Ultimately the characteristics of the thin film dictated the shrinkage of the supported thin film structure, and results obtained during this quarter enabled further minimization of membrane stress during sintering.

Finally, initial SEM results suggested that many of the thin film samples contained pores in the membranes surface. However, SEM cross-section analyses of these samples indicated that the voids actually were bubbles that had burst, leaving a very thin dense residual film.

Task 5 *Construction and Evaluation of Prototype Hydrogen Separation Unit*

No actions were performed on this task during this reporting period.

Task 6 *Membrane-Promoted Conversion of Alkanes to Olefins*

During this reporting period, preparation of calibration curves for GC analysis of reactants and products for propane dehydrogenation was initiated, and preliminary catalyst compositions were outlined.

SUMMARY AND CONCLUSIONS

Conclusions based on the work performed during this quarter are summarized as follows:

- Permeation of H₂ increased significantly as the membrane thickness decreased for a selected cermet composition. A maximum permeation rate of ~0.5 mL/min/cm² was achieved for a 0.8-mm thick membrane at 950°C.
- The improvement in permeation exceeded the 1/thickness dependence predicted by the model.
- Highest permeation rates were achieved for cermet membranes without any added catalyst.
- Cermet membranes sintered under more reductive conditions had more oxygen vacancies that distorted the ABO₃ lattice and lead to inhibited grain growth and weaker grain boundaries. These factors produced asymmetry, which likely decreases H₂ permeation by creating unequal lattice sites along the proton conduction pathway.
- A wide range of ceramic and cermet membrane compositions appeared to be unstable in the presence of H₂S. Desulfurization of feedstream gases likely will be necessary prior to entering a H₂ separation unit based on these materials.
- Stresses induced in thin film membranes during sintering can be minimized by controlling the characteristics of the support material.

OBJECTIVES FOR NEXT REPORTING PERIOD

Specific objectives for the next quarter are summarized as follows:

- Continue testing of multi-phase ceramics and cermets, including cermets containing hydrogen transport metals.
- Perform SEM analysis on cermet membranes to determine sample cross-section homogeneity.
- Further refine manufacturing of selected membrane compositions
- Perform hydrogen separation analysis on supported thin film membranes.
- Continue catalyst testing
- Continue membrane stability studies.
- Screen catalysts for propane dehydrogenation.

TIME LINES

The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

